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Kinetic Analysis of High-Nitrogen Energetic Materials Using Multivariate Nonlinear Regression

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ABSTRACT

New high-nitrogen energetic materials were synthesized by Hiskey and Naud. J. Opfermann reported a new tool for finding the probable model of the complex reactions using multivariate non-linear regression analysis of DSC and TGA data from several measurements run at different heating rates. This study is to take the kinetic parameters from the different steps and discover which reaction step is responsible for the runaway reaction by comparing predicted results from the Frank-Kamenetskii equation with the critical temperature found experimentally using the modified Henkin test.

INTRODUCTION

Our group has been interested in high nitrogen energetic materials and Hiskey, et. al. have synthesized a number of new compounds that are possible propellant ingredients, gas generators, and low smoke pyrotechnics. For safety and storage use, we need to understand their methods of decomposition; hence we need to study their kinetics. One of the compounds that shows promise is 3,6-bis(1H-1,2,3,4-tetrazol-5-ylamino)-1,2,4,5-tetrazine (BTATz) (1). It has a molecular formula of $C_4H_4N_{14}$ and contains 79wt% nitrogen. It is of interest as an ingredient in a low signature rocket propellant or gun propellant because primarily N_2 gas is produced during decomposition. Another compound is 3,3'-azobis(6-amino-1,2,4,5-tetrazine) (DAAT) or $C_4H_4N_{12}$ with 76wt% nitrogen (2). It forms planar sheets and has a high positive heat of formation. This compound could be another valuable propellant ingredient. DAAT has the tetrazine ring system; but instead of tetrazole substituents, it has an azo link between two rings, which can be a trigger for decomposition.

One of the first safety tests done on new explosives is DSC to find the temperature of onset of exothermic behavior. But to predict the results of a larger sample, kinetic parameters, thermal conductivity, heat of reaction, density, and size and shape of the larger sample are necessary to model the critical temperature. The definition of critical temperature (T_m) is the lowest isothermal surface temperature at which a specific material of a specific size and shape will self-heat catastrophically (3). The kinetics of solid energetic materials are almost always complex multiphase reactions with slow reactions taking place in the solid, resulting in products that interact with the explosive to lower the melting point or act as catalysts to increase the reaction rate in the explosive (4). Once the reactions produce heat, the size and thermal conductivity of the piece becomes important. Below the critical temperature, the size and shape allow the heat to dissipate to the surface, and a low temperature gradient is established. Decomposition is occurring below the critical temperature, but the heat produced

is able to move to the surface without increasing the temperature at the center. However, at a higher surface temperature $>T_m$, the gradient becomes steeper, and as the temperature increases the reaction rate increases according to the Arrhenius reaction rate model $K = Ae^{E_a/RT}$. Phase changes from solid to liquid can also occur as the temperature at the center of the sample rises. One single model may be used to simulate part of the reaction, but not all (4).

For safe handling of explosives, we need to know the kinetic parameters of the reaction that causes the runaway catastrophic event. But for storage, we are also interested in the slow reactions, which are taking place at lower temperatures that may degrade the performance. The standard small test used to find the critical temperature for a specific size and shape of a new explosive or mixture is called the modified Henkin critical temperature test (3). It uses small pressed slabs of explosive enclosed in aluminum shells and subjects each to an isothermal temperature bath to find the lowest temperature that will give a runaway reaction. Frank-Kamenetskii devised an equation that uses the physical properties of the material plus kinetic parameters and shape factor to model the critical temperature of a sample that was heated isothermally on the surface (5).

$$\frac{E}{T_m} = R \ln \left[\frac{a^2 \rho Q Z E}{T_m^2 \lambda \delta R} \right] \quad (1)$$

Where: R is the gas constant,

a is the radius of a sphere or cylinder or the half-thickness of a slab,

ρ is the density,

Q is the heat of reaction during the self-heating process,

Z is the pre-exponential,

E is the activation energy from the Arrhenius expression,

λ is the thermal conductivity,

δ is the shape factor (0.88 for infinite slabs, 2.00 for infinite cylinders and 3.32 for spheres).

The correct activation energy and pre-exponential of the runaway portion of the total reaction when used with the chemical and physical properties of the sample will calculate the experimental critical temperature within a few degrees (3). However, the total reaction may include other steps including sublimation, melting, autocatalytic reactions, diffusion, and decomposition at different rates from the reaction step that causes the catastrophic runaway reaction. It is desirable to know the other steps to understand the total behavior of the explosive. In kinetic analysis of a multistep process, the products of one step can be reactants of another step with the possibility of endothermic as well as exothermic reactions and linear as well as branched paths. Vyazovkin and Wight in their review of solid-state kinetics offer the model-free approach that uses the isoconversional principle as the best method for multistep solid-state reactions. They applied the method to the thermal decomposition of ammonium dinitramide and showed the change in activation energy as a function of degree of conversion. The complexity of the reaction mechanism is revealed by the changes of activation energy as the reaction proceeds. They refer to other experiments that indicate the presence of at least two competing reaction pathways (6).

For single step processes an analytical solution is possible to describe the kinetics; but in complex multistep processes, the differential equation: $de/dt = -U(t,T,e,p)$ becomes a system of differential equations, for which the separation of variables is no longer possible and hence no analytical solution. However, desktop computers have the capability to do regressive analysis of complex differential equations in a reasonable time. J. Opfermann has developed a code for kinetic analysis using multivariate non-linear regression (7). First a Friedman model-free analysis (8) is applied to the data, which was taken from at least 3 ramp rates by DSC or TGA of the reacting material. The appearance of the analysis shows how the isoconversional lines are compared with the data. If the slope of the experimental points is greater than the slope of the isoconversional lines, then the reaction is autocatalytically activated. If the slope is less, then diffusion processes control the initial reaction. If the data corresponds to the lines, then an nth order reaction is the model applied. If the values for activation energy and pre-exponential are constant throughout the reaction, then the reaction may have one step, but if there are changes, it is a multistep reaction. Regression analysis of a series of multistep models may be necessary before a good fit to the data is found. A round robin reported by Flammersheim evaluated this method with good results (9).

It is best to check any result of kinetic calculations with results from other experiments. After finding a model and kinetic parameters by the nonlinear regression process, it was compared with experimental results from the modified Henkin test (4). The kinetic parameters that predict the Henkin critical temperature are used to calculate the critical temperature for a 2-in. diam right circular cylinder to find a safe temperature for pressing.

EXPERIMENTAL

DSC's were run on TA Instrument 2920 DSC with $30 \text{ cm}^3 \text{ min}^{-1}$ nitrogen gas flow at three or more ramp rates, for example 1°C min^{-1} , 3°C min^{-1} , and $10^\circ\text{C min}^{-1}$. The 1.0-mg samples were enclosed in hermetically sealed aluminum cell with a pinhole of $0.19 \pm 0.02 \text{ mm}$.

TGA's were run on TA Instruments 2950 with flow of nitrogen gas of $40 \text{ cm}^3 \text{ min}^{-1}$. at ramp rates of 6°C min^{-1} , 3°C min^{-1} , 1°C min^{-1} . The 3 to 5-mg samples were spread on the surface of an open platinum pan.

Henkin critical temperature tests were run on 40-mg samples enclosed in 6.63-id aluminum shells, which were sealed by pressing a beveled seal onto the sample to form a thin slab of material. The assembly is dropped remotely into an isothermal heated metal bath, starting at a temperature indicated by exothermic activity on the DSC, and timed until a "pop" is heard. The temperature of the bath is lowered until no "pop" is heard during three times the length of time of the lowest temperature runaway reaction. This temperature is the critical temperature for this size and shape of explosives.

The kinetic multivariate non-linear regression code used was the Netzsch Advanced Kinetics code. The ASCII data from DSC or TGA analysis from at least three ramp rates with 10 times the difference in rate was input into the code. Isothermal data can also be used. The code includes model free, linear, and

nonlinear methods. Predictions from the results are also included. After loading the data the Friedman isoconversional analysis is applied to the data to indicate type of beginning reaction model and how many steps should be tried. Results from Friedman analysis are used as starting parameters for nonlinear regression analysis.

RESULTS AND DISCUSSION

The new high nitrogen propellant ingredient BTATz was analyzed both by TGA and DSC. The initial step was different due to the difference in the configuration of the sample holder. The MTDSC reversing trace showed a melting endothermic transition during decomposition, while the TGA showed slow weight loss at temperatures leading to the decomposition temperature probably due to sublimation. Also observed, but not understood, was the deflagration of the sample at 10°C/min ramp rate. At ramp rates lower than 6°C min⁻¹, the weight loss was smooth with a change in slope after 35wt% loss, but not reaching zero even at 450°C. Figure 1 shows the fit found using nonlinear multivariate regression method. DAAT exhibited the same behavior.

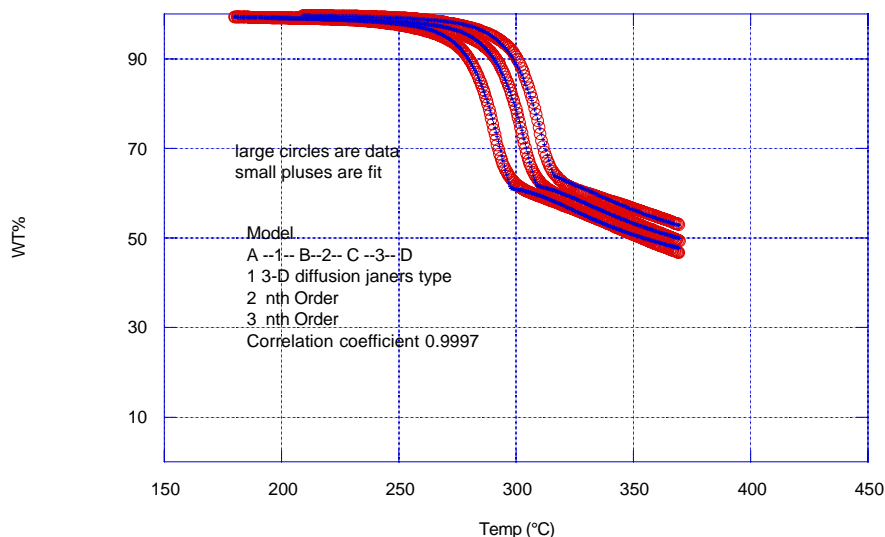


Figure 1 - BTATz results from TGA at Ramp Rates of 6°C min⁻¹, 3°C min⁻¹, and 1°C min⁻¹.

The major reaction during the loss of 35wt% of BTATz predicts the result from the Henkin test, but the beginning step rather than the main reaction of DAAT predicts the Henkin of the DAAT. This is probably due to the azo linkage decomposition. This step is only 0.023 of the conversion, but has lower activation energy than found for the first step for BTATz. Tables 1-3 lists the parameters used in the Frank-Kamenetskii equation, the calculated, and the experimental Henkin critical temperature for BTATz and DAAT.

Table 1. Calculated and Experimental Critical Temperatures of BTATz by TGA

Kinetic Parameters	Density (g/cm ³)	Heat Cond. (cal cm ⁻¹ s ⁻¹ °C ⁻¹)	Size (cm)	Q (cal)	Calc T _m (°C)	Exp.T _m (°C)
Step 1 E1 (calmol ⁻¹)	34952	1.3	0.0006	0.047	335	344
Step 1 A1	2.57 x 10 ¹⁰					303
Step 2 E2	64355				305	303
Step 2 A2	1.097 x 10 ²²					
Step 3 E3	87922				332	303
Step 3 A3	2.34 x 10 ²⁹					

Table 2. Calculated and Experimental Critical Temperatures of BTATz by DSC

Kinetic Parameters	Density (g/cm ³)	Heat Cond. (cal cm ⁻¹ s ⁻¹ °C ⁻¹)	Size (cm)	Q (cal)	Calc T _m (°C)	Exp T _m (°C)
Step 1 E1 (calmol ⁻¹)	70083	1.3	0.0006	0.047	335	283
Step 1 A1 (s ⁻¹)	1.603 x 10 ²⁵					303
Step 2 E2	59570				304	303
Step 2 A2	2.0 x 10 ²⁰					
Step 3 E3	53927				298	303
Step 3 A3	2.59 x 10 ¹⁸					

Table 3 Calculated and Experimental Critical Temperatures of DAAT by TGA

Kinetic Parameters	Density (g/cm ³)	Heat Cond. (cal cm ⁻¹ s ⁻¹ °C ⁻¹)	Size (cm)	Q (cal)	Calc T _m (°C)	Exp T _m (°C)
Step 1 E1 (calmol ⁻¹)	58585	1.37	0.0006	0.044	425	283
Step 1 A1 (s ⁻¹)	5.16 x 10 ²⁰					293
Step 2 E2	56405				317	293
Step 2 A2	4.57x 10 ¹⁸					
Step 3 E3	96551				317	293
Step 3 A3	1.86 x 10 ³³					

CONCLUSIONS

Determining the kinetics parameters from the nonlinear multivariate regression of multiple ramp rate analysis of energetic materials gave a picture of the changes in the solid state decomposition of these new compounds that showed different decomposition steps for enclosed verses open container modes of decomposition. For BTATz, the code calculated kinetic parameters for the main decomposition step from both DSC and TGA data that gave a T_m calculated with the Frank-Kamenetskii equation that agreed very well with experimental T_m.

DAAT and BTATz have very similar DSC and TGA decomposition temperatures but have very different initial decomposition kinetic parameters even for the same model after regression analysis. The first step of DAAT had a lower calculated T_i which agreed with its lower T_m experimentally. The amount of energy in its first step is low and only was observed to cause the seal to push up the tube with a soft pop in the Henkin critical temperature test. It did not break a hole in the aluminum tube. Even though it did not do much damage, it could cause the sample to deflagrate as was seen at higher ramp rates on the TGA at $10^{\circ}\text{C min}^{-1}$. Additional larger experiments will be necessary to discover if this initial reaction will cause a catastrophic runaway reaction at a lower temperature.

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